Effect of laser annealing on optical properties of ZnCdSe/ZnSSe quantum well heterostructures

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ZnSe-based nano-size structures have recently become objects of extensive research activity. In particular, the advanced molecular beam epitaxy (MBE) allows fabrication of high-quality multiple-layer heterostructures grown on a GaAs substrate and including ZnCdSe/ZnSSe quantum wells (QWs) and superlattices (SLs). Nevertheless, the techniques of lateral pattering, resulting in homogeneous arrays of lower-dimensional systems (quantum dots (QDs) or quantum wires) are still not sufficiently developed. The principle problem is supposed to be a simplicity of extended defects formation, which can be activated by any external perturbation during the post-growth process. Note that even application of a standard photolithography for formation of the device functional elements (e.g. narrow laser stripes) usually introduces additional defects, disturbing optical characteristics of these soft-lattice structures [1].

In this paper we study an alternative method of lateral pattering, based on the effect of local interdiffusion induced by a focused laser beam. This technique was previously applied to a single GaAs/AlGaAs single-QW heterostructure, resulting in creation of optically active QDs with perfectly controlled lateral sizes [2]. However, as applied to the wide bandgap II-VI structures, this approach meets a specific problem. The treated layer should be thick enough to provide efficient heating by absorbing the laser emission. Otherwise, most of the light pass the region of interest, heating the thick substrate. This problem is automatically solved in GaAs-based structures by using blue-green lines of a cw Ar⁺ laser, efficiently absorbed directly in ~ 1000 Å thick AlGaAs cap layer. As for the strained (Zn,Cd)(S,Se) epilayers on GaAs, the only compound allowing pseudomorphic growth of a reasonably thick layer is the ternary ZnS_xSe_{1-x} solid alloys with x = 0.04-0.10 satisfactorily latticematched to a GaAs substrate. These alloys possess the room-temperature band gap of about 450 nm and, therefore, are transparent for all blue and green lines of an Ar⁺ laser. Most of other available cw laser lines of reasonable power are in the ultraviolet (UV) region, but the UV high-energy quanta are generally supposed to stimulate formation of point defects. We believe that just this assumption has determined the lack of data published (at least, to our knowledge) in the field of laser-induced pattering of the wide-gap II-VI heterostructures.

To overcome this problem, we have used the concept of alternatively-strained SL growth, previously applied to fabrication of extremely thick ZnCdSe/ZnSSe QW structures lattice-matched to GaAs as a whole [3]. The studied structure was grown by MBE on a (100) GaAs substrate at 280°C, using the only shutter-operation technique, as described elsewhere [4]. The sample comprises a 30-period (17 nm-ZnS $_{0.08}$ Se $_{0.92}$ /5 nm-Zn $_{0.82}$ Cd $_{0.18}$ Se) multiple QW (MQW) structure with a total thickness of 0.66 μ m, embedded in Zn $_{0.92}$ Mg $_{0.08}$ So $_{0.09}$ Se $_{0.91}$ quaternary claddings. Such a structure allows, in principle, local heating by the 488 nm Ar $^+$ laser line with a control over the heating volume in all three dimensions. In the lateral directions, the minimum beam focus size is determined by the diffraction limit as about half of the wavelength, whereas in the vertical direction the heat localization is achieved by the selective light absorption within the MQW region. The

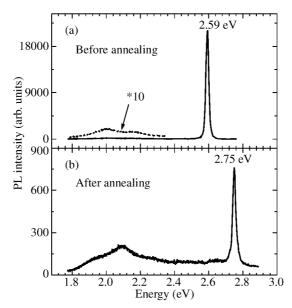


Fig. 1. PL spectra measured at 77 K in unannealed (a) and annealed (b) samples.

dominant expected effect is interdiffusion of the involved elements during the exposure to laser light, modifying the band gap energy (E_g) and, hence, the optical and electronic properties. Thus, the Zn-Cd interdiffusion in the ZnCdSe/ZnSSe QW is to result in an increase of the band gap. In the particular structure studied the local band gap enhancement can be as high as 160 meV, provided the complete intermixing between the well and barrier materials. Using the interdiffusion parameters published for this system in Refs. [5] and [6], one can calculate that observation of the noticeable effect (the 10–20 meV shift of E_g due to about one minute exposure to the laser light) requires local heating over 500–600°C. Simple estimations show that in the sample geometry used this temperature can be achieved by applying the cw laser power density of about 1 kW/cm², which can be readily obtained experimentally.

However, the principle problem is whether it is possible to stimulate the large enough changes of E_g without inducing additional defects. To elucidate this question we performed a series of laser annealing experiments changing both the laser power and the exposure time. Figure 1(a) and (b) demonstrate, respectively, photoluminescence (PL) spectra for two extreme cases—unannealed sample and a sample annealed under the conditions resulting in visible degradation of the structure capping layer. To reach this effect we annealed the structure for 5 minutes in air by applying the laser power density of about 1.5 kW/cm². PL measurements were made at 77 K with a 325 nm line of a 1 mW He-Cd laser. An iodine tungsten lamp emission dispersed by a single-grating monocromator was used for PL excitation (PLE) measurements.

The resulting effect of the blue shift is well pronounced, being close to a maximum possible value of about 160 meV. The annealing also leads to a decrease of the band-edge PL intensity (by 25 times). The formation of additional defects in the annealed sample is also confirmed by a rise of a red PL line close to 2.1 eV, which is known as a measure of structural perfection. However, the PL linewidth increases only slightly (from 20 to 25 meV), indicating that even the extreme annealing conditions still leave the structure optically active.

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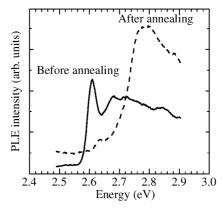


Fig. 2. PLE spectra measured at 77 K in unannealed (solid curve) and annealed (dashed curve) samples. The detection energy is 2.0 eV.

The effect of annealing also reveals itself in the PLE spectra of the samples shown in Fig. 2. The laser treatment results in a drastic blue shift of the fundamental band-edge, followed by broadening and disappearance of the band-edge excitonic line.

In conclusion, we designed and fabricated a (Zn,Cd)(S,Se) MQW heterostructure allowing control over the optical and electronic properties by an exposure to 488 nm Ar⁺ laser line. The laser-induced intermixing of elements results in a significant band edge blue shift with a moderate level of introduced defects. By controlling the light pattern on the sample surface this technique allows lateral pattering for fabricating e.g. ultra-narrow stripes or dot-like objects for optoelectronic devices.

This work has been supported in part by the RFBR, the program of MS of RF "Physics of solid-states nanostructures" as well as the Volkswagenstiftung.

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